SYNOPSIS

The lubricity of an emulsion is related to the transport, of oil and surfactant to the metal substrate. The oil droplets if they can be transported such, wet the steel substrate and give microhydrodynamic lubrication. The surfactant molecules as and when assembled on the substrate provide hydrophobicity and reduce the surface potential of the substrate, both aid in enhancing lubricity.

In this thesis we first investigate the lubricity of an anionic surfactant sodium oleate self assembled ex-situ on a polished steel substrate. The lubricity of the assembly is found to be related to the contact pressure, above a critical pressure the molecules react chemically with the substrate to yield a tribo-film which when sheared at contact gives a low value of coefficient of friction.

The thesis then explores the transport of oil to the substrate. In this two problems are investigated; (1) the force regime between an oil droplet and steel in water medium and the resulting disjoining pressure and (2) the ability of free oil droplets to be transported naturally to the substrate against gravity.

The present thesis is constructed based on the hypothesis that the transport of oil to a substrate in water medium is related to the force regime which exists between oil and the substrate; the stronger the attraction the easier is the transport. We simulate this interaction by allowing a 600 nm diameter silica probe smeared with an oil film, mounted on an atomic force microscope (AFM) cantilever to approach a solid substrate in water medium. We attempt to identify the force components such as DLVO, capillary, hydration and hydrophobic forces by integrating the force estimates and fitting the sum with those measured in the experiment. To create a variety of force regimes, and to validate the theoretical estimation and force classification by observing the fit between the experimental and theoretical estimates, the experimental electrical and physical parameters were varied. Given the success of this benchmarking exercise we examine the force regime when the substrate is steel, to find that the DLVO and capillary forces are predominent, the overall force regime remains repulsive even in the presence of capillary forces.

There is a thin water film which intervenes between an oil droplet and the steel substrate. For good lubricity this film needs to be disjoined and repelled by oil. The present work shows that the electrical status, of the substrate and the oil droplet, the ionic state of the water medium and wettability of the substrate play important roles in determining the disjoining pressure.

The oil droplets suitably agitated in an emulsion was found to have a bimodal size distribution. The average size in each mode is critically dependant on the anionic surfactant concentration. A critical concentration gave the highest small-/large droplet volume ratio (Vs/Vb). The surface charges of the droplet and the substrate were measured by dynamic light scattering and pH-titration methods respectively. Given these estimates and the droplet size it was possible to set up the well known DLVO force interaction to show that at a critical surfactant concentration the volume ratio Vs/Vb is maximum and the force of attraction between the droplet and the substrate is also maximum at the same concentration. Given this condition for the easiest transport of oil to the substrate, it is shown that the friction coefficient between a steel ball sliding against a steel substrate, is also minimum at the critical surfactant concentration.

To reduce the repulsion and to bring the interaction strongly into an attractive mode we next planned to use surfactants in the oil medium. However to do that it was essential for us to map the diffusion of surfactant molecules through the oil/water interface. Two anionic surfactants of disparate HLB values (HLB = 1, highly soluble in oil; HLB = 18, highly soluble in water) were used to study the phenomenon. (1) A droplet of water was made pendant in an oil reservoir and (2) the water droplet was posited on the substrate in oil, by gravity. The deformation of the droplet due to the diffusion of the surfactant across the interface was recorded to give the variation of interfacial tension with time. The surfactant sodium oleate, insoluble in oil and highly soluble in water was found to yield the lowest (amongst all test configurations) interfacial tension, when it was initially dispersed in oil. This configuration was also found to provide the best hydrophobicity and the most appropriate condition for the replacement of water by oil from the substrate.

Now given the fact that the droplet size and solubility of the surfactant in a medium play important roles in controlling the transport of oil to the substrate and the disjoining pressure, we study the influence of the two anionic surfactants of disparate HLB values on the disjoining pressure. The study shows, essentially, that an oil insoluble surfactant dispersed in oil is able to diffuse readily through the oil/water interface into water to be adsorbed by the substrate. This lowers the surface potential and generates a strong attractive force between the oil and the steel substrate. This effect is unfortunately lost if the emulsion is stored for a long period of time. Tribological experiments, where a steel ball slides on a steel substrate gives a low coefficient of friction when the surfactant is insoluble in oil (HLB = 18) compared to what is achieved when the surfactant is soluble in oil (HLB = 1).

In this work we arrive at the four essential conditions required for an emulsion to be a lubricating fluid, in a steel on steel tribological interaction:

1. The surfactant concentration should be controlled to give large small to high droplet volume ratio.

2. The anionic surfactant should be insoluble in oil and soluble in water and should be dispersed apriori in oil.

3. The tribological experiments should be done with freshly dispersed surfactant as long exposure of the substrate to the molecules diffusing through water creates an excess on the substrate which may be detrimental to tribology.

4. A substrate potentially wettable by oil is lubricated well by emulsion as it allows the development of long range capillary attraction force between the oil and the substrate.